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(54) Title: BF_3-TERTIARY ETHERATE COMPLEXES FOR ISOBUTYLENE POLYMERIZATION

(57) Abstract

Disclosed herein are boron trifluoride etherate complexes in which the ether of the complex has at least one tertiary carbon bonded to an ether oxygen. The etherates are useful for polymerizing a one-olefin or mixtures thereof, preferably comprising isobutylene, whereby the resulting polymer contains a high percentage (80-100 %) vinylidene character.

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BF_3-TERTIARY ETHERATE COMPLEXES FOR ISOBUTYLENE POLYMERIZATION

Field of the Invention

The present invention relates generally to BF_3-etherate complexes useful for polymerization of 1-olefin containing feedstocks. More particularly the invention is directed to BF_3-etherates in which the ether of the BF_3-etherate has at least one tertiary carbon bonded to an ether oxygen, and to a process for polymerizing feedstocks comprising isobutylene wherein the BF_3-tertiary etherate is the catalyst. The BF_3-tertiary etherates of the present invention and the polymerization process employing them are suitable for manufacturing polybutene having a very high percentage (80 to 100%) of vinylidene olefin.

Discussion of the Prior Art

Generally speaking, polymerization of 1-olefin containing feedstocks using catalysts such as aluminum chloride and boron trifluoride is disclosed extensively in the patent and technical literature. It is well known that the termination step in isobutylene polymerization results in a "terminal" double bond which imparts desired reactivity to the polymer for subsequent reactions, such as epoxidization or reaction with maleic anhydride. However, a problem exists in that the termination step can place the terminal double bond in a highly reactive external 1, 1-disubstituted position (hereafter "vinylidene"), or in a much less reactive internal tri-substituted or tetra-substituted position. These three possible terminal double bond positions are shown below.

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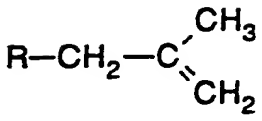
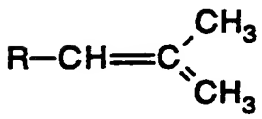
Vinylidene



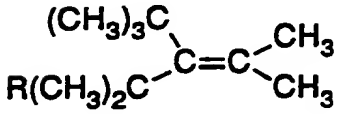
(R = polymer residue)

Tri-Substituted



(R = polymer residue)

Tetra-Substituted



(R = polymer residue)

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Referring to this problem, Samson U.S. Patent 4,605,808 states that the product obtained upon conventional polymerization of isobutylene is generally a mixture of polymers having a high proportion of internal versus external (vinylidene) unsaturation due to "in situ" isomerization of the more highly reactive vinylidene double bond to the less reactive internal positions. The diminished reactivity of the hindered internal tri-substituted or tetra-substituted double bond is most notably observed in the manufacture of the valuable intermediate polyisobutenyl succinic anhydride ("PIBSA") which is obtained by reaction of maleic anhydride with polybutene. PIBSA is a very important intermediate in the manufacture of fuel and lubricant additives. The lowered reactivity of polybutene due to the presence of substantial internal olefinicity reduces the yield of PIBSA when the polymer is reacted with maleic anhydride and thus dictates higher usage of polybutene than would otherwise suffice if the polybutene consisted mainly of vinylidene olefin.

Given the above problem, it has long been an object of research in the area of polybutene manufacture of improve the reactivity of polybutene, particularly its reactivity toward maleic anhydride, by identifying catalysts or catalyst systems capable of polymerizing isobutylene such that the resulting polybutene has the highest possible percentage of vinylidene double bonds.

A number of patents have sought to address this very problem. Nolan U.S. Patent 3,166,546 discloses a vapor phase process for isobutylene polymerization which requires using a mixture of gaseous boron trifluoride and sulfur dioxide under specified conditions. The patent states that sulfur dioxide directs the polymerization reaction such that substantially all of the polybutene has vinylidene unsaturation. In column 1 of the patent, it is stated that the boron trifluoride catalyst requires a small amount of water, alcohol, carboxylic acid, mineral acid or ether to initiate the catalyst. However, there is no suggestion for the use of BF_3-tertiary etherate complexes. Moreover, the sulfur dioxide process does not appear to be commercially viable.

In later work using BF_3 catalyst, Boerzel et al. U.S. Patent 4,152,499 disclosed that BF_3 mainly favors the formation of polymer having the reactive double bond in the vinylidene position if a short polymerization time (3 to 5 minutes) is strictly maintained.

Most recently, Samson U.S. Patent 4,605,808 discloses isobutylene polymerization using a preformed boron trifluoride/alcohol complex and contact times in the range of 8 to 70 minutes, as a means of obtaining a high

percentage (at least 70 percent) of vinylidene content in the resulting polybutene polymer.

While the patents cited above dealing with BF_3 catalysis are indicative of progress toward the achievement of a highly reactive (high vinylidene) polybutene, a number of problems remain to be solved. First, the teachings of these patents place strict restraints on the contact time for the catalysts. For example, in the case of the above cited Boerzel Patent, a contact time of 1 to 10 minutes is claimed but 3 to 5 minutes is the preferred range. If the brief contact times are not maintained, the desired high levels of vinylidene unsaturation cannot be achieved given the tendency of the vinylidene double bonds in the polymer to isomerize in the presence of the catalyst to the less reactive internal type double bond.

To some extent, this problem may have been alleviated in the Samson '808 patent teaching use of a preformed boron triflouride/alcohol complex with contact times of 8 to 70 minutes to obtain polymer having at least 70% vinylidene content. Nevertheless, it is desired to increase even further the percentage of vinylidene content obtainable in the polymer, while at the same time eliminating or minimizing the dependency of such outcome upon rigorously maintained contact times.

Inasmuch as the present invention relates generally to isobutylene polymerization in the presence of boron triflouride etherate complexes, a number of additional literature references and patents, in addition to those already discussed above, are believed to be of general relevance although they fail to address the problem sought to be overcome by the present invention and can be readily distinguished. For example, Dornte U.S. Patent 2,559,062 discloses isobutylene polymerization using boron trifluoride complexed with di-n-butyl ether, halogen-substituted dialkyl ethers, aryl-alkyl mixed ethers, nirtoaryl ethers, cyclic ethers and unsaturated ethers. The patent notes that the types of ethers used for complexation with BF_3 may not be indiscriminately selected, and makes no mention of tertiary etherates in which a tertiary carbon is bonded to the ether oxygen.

Stevens et al. U.S. Patent Nos. 2,588,425 and 2,591,384 disclose preparation of an isobutylene polymer consisting almost exclusively of tetraisobutylene or triisobutylene. The tetramer or trimer is prepared from isobutylene at 0 C to 55°C in the presence of a boron trifluoride ether complex. The ether compounds disclosed by Stevens do not include tertiary ethers.

Montgomery et al. U.S. Patent 2,559,984 teach the use of aluminum chloride or boron fluoride catalysts complexed with organic compounds, but the patent mentions ethers only in the context of aluminum chloride catalysts.

Ikida U.S. Patent 2,777,890 discloses the use of a boron trifluoride diethylether complex as a catalyst for polymerization of butadiene-1, 3.

Throckmorton U.S. Patent 3,962,375 discloses boron trifluoride complexed with ethers of the formula ROR' where R and R' represent alkyl, cycloalkyl, aryl, alkyaryl, arylalkyl radicals containing from 1 to about 30 carbons.

Serniuk U.S. Patent 2,780,664 discloses preparation of a drying oil by contacting a mixture of 75 parts by weight of butadiene and 25 parts by weight of isobutylene in the presence of boron trifluoride ethylether complex.

Geiser U.S. Patent 3,006,906 discloses copolymerization of isobutylene with a tetra-substituted alkylene diamine in the presence of a boron trifluoride ethylether complex.

Holmes U.S. Patent 2,384,916 discloses a method of producing high molecular weight iso-olefin polymers using boron trifluoride catalysts promoted with ethylether, normal propylether, isopropylether, normal butylether, methyl normal butylether and isoamylether. The use of boron trifluoride: tertiary ether complexes to obtain polybutene having high levels of vinylidene unsaturation is no where disclosed or suggested in this patent.

Finally, it should be noted that early work by Evans et al. determined the necessity in BF_3 catalysis of a complexing agent able to donate a proton. Evans discovered that no polymerization will occur when pure diisobutylene is exposed to BF_3 unless a trace amount of moisture is present. This finding has generally led to the acceptance of a cationic mechanism, and therefore the requirement of a proton source, for both BF_3 and $AlCl_3$ catalysis. The early work of Evans in conjunction with his associates, Meadows and Polanyi, is described in Nature (1947) 160, page 869; J. Chem. Soc. (1947) 252; and Nature (1946) 158, page 94. To date, the cationic mechanism ascribed to BF_3 and $AlCl_3$ catalysis requiring proton donation to initiate polymerization is widely accepted.

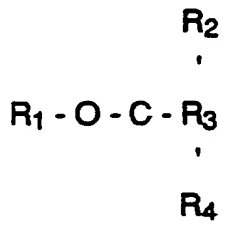
To the best of my knowledge the patents and literature references discussed above with respect to the use of BF_3-etherate complexes are not addressed to the attainment of high vinylidene content in polybutene and do not teach tertiary etherates capable of achieving that result. On the contrary the BF_3 ether complexes taught in these early patents are inactive unless they are activated with a proton source. Under the accepted cationic mechanism for

such polymerization the actual BF_3 catalyst in the presence of such a proton source acts as a Lewis acid having a strong tendency to isomerize the vinylidene double bonds to the less reactive internal double bonds and to cause skeletal rearrangements and branching of the polybutene formed during the polymerization reaction. The latter is a disadvantage in that a highly linear polymer is generally preferred in lubricant additive manufacture.

In view of the foregoing discussion of the prior art, an object of the present invention is generally to provide an improved BF_3 catalyst system useful in the preparation of polybutene having a high percentage of vinylidene unsaturation. Other objects will be apparent hereinafter to those skilled in the art.

Summary of the Invention

I have now discovered an improved boron trifluoride catalyst system for use in the polymerization of 1-olefin containing feedstocks. The catalyst system comprises a BF3-etherate complex in which the ether has at least one tertiary carbon bonded to an ether oxygen. The tertiary ether can have the general formula:



where R_1 is C_1 to C_{20} hydrocarbyl or halo-substituted hydrocarbyl and R_2, R_3 and R_4, the same or different, are selected from the group consisting of (1)-CH_2R' where R' is H, halogen, or C_1 to C_{20} hydrocarbyl or halo substituted hydrocarbyl; (2)-CH=R" where R" is C_1 to C_{20} hydrocarbyl or halo substituted hydrocarbyl; and (3)-C≡R" ' where R" ' is C_1 to C_{20} hydrocarbyl or halo substituted hydrocarbyl. Preferred tertiary ethers for use in preparation of the BF_3-etherate complexes of the present invention are those in which R_2, R_3 and R_4 in the above formula are methyl, and R_1 is C_1 to C_{10} hydrocarbyl. Particularly preferred are the alkyl tert-butyl ethers, e.g., methyl t-butyl ether, n-butyl t-butyl ether, isopropyl t-butyl ether, di-tert-butyl ether, ethyl tert-butyl ether, pentyl tert-butyl-ether,1, 1'-dimethylbutyl methylether, etc.

As a method, the present invention is directed to a process for polymerizing a feedstock comprising 1-olefin which process comprises the step of contacting the feedstock with a BF_3-tertiary etherate as described

above at -100 to +50°C. The process is suitable for polymerizing isobutylene to obtain commercial grade polybutene having high percentages of vinylidene olefinicity (i.e., 80 to 100%).

A principle advantage of the BF_3-tertiary etherate complexes of the present invention is their ability to produce polybutene polymer having higher percentages of vinylidene unsaturation (80 to 100%) than obtained using the BF_3-catalysts of the prior art (i.e., Boerzel U.S. Patent 4,152,499 and Samson U.S. Patent 4,605,808) which, by comparison, are taught to be capable of producing vinylidene contents in the range of only about 60 to 90%.

The etherates of the present invention also compare favorably to the BF_3-alcoholate complexes of Samson in their ability to produce higher molecular weight polymer at a given temperature.

Still a further advantage is that longer residence times are acceptable in the BF_3-etherate catalyzed polymerization of the present invention. Residence times of 10 minutes to 3 hours (or greater) can be used depending upon temperature, catalyst concentration and desired molecular weight.

Further advantages include the fact that the BF_3-etherates of the present invention are more active than BF_3-alcohol complexes and show greater selectivity for isobutylene than conventional $AlCl_3$ catalyst. This latter advantage reduces the stripping required for the raw polybutene product..

Finally, in comparison to aluminum chloride catalyzed polymerization, the polybutene product resulting from the BF_3-tertiary etherates of the present invention is more linear (less branching and skeletal rearrangements) and is consistently colorless.

Surprisingly, unlike the prior art BF_3 catalyst systems which require a protic source (i.e., water, alcohol, mineral acid, etc.) to initiate polymerization, the BF_3-tertiary etherate complexes of the present invention do not require protic initiation. In fact, they are found to perform optimally in terms of high vinylidene content, using feeds that are essentially completely free of water or other protic species capable of complexing with the BF_3 by displacement of the tertiary ether. As the presence of water or other proton donating species in the feed or reaction zone increases, even slightly, the ability of the BF_3-tertiary etherates to produce high vinylidene falls off dramatically. Therefore the preferred feedstock for use in the present invention should be as anhydrous as possible, preferably containing no greater than about 1 to about 10 ppm water. However, feeds having 10 to 20 ppm H_2O can be used without seriously impairing the advantages of the present invention. At levels greater than about 20 ppm H_2O, the BF_3 etherates of the present invention may perform worse

than the prior art BF_3 catalysts measured in terms of the ability to produce high vinylidene content in the polymer product.

Without any intention to be bound to a particular theory, it is believed that the advantages noted above, namely higher vinylidene content, longer residence times, higher molecular weight polymer, more linear polymer, etc., result from the fact that the BF_3 tertiary etherates of the present invention do not require protic initiation for polymerization to take place. Protic initiation, characteristic of a cationic mechanism for isobutylene polymerization results in a reaction environment which is highly acidic due to the proton donation by the active catalyst species, such active species being a complex of the protonic entity (for example water) and the BF_3. The acidic reaction environment characteristic of proton initiated polymerization is believed the principle cause underlying isomerization of terminal vinylidene unsaturation to the less desired ad less reactive internal unsaturation. Acidity at the onset of polymerization resulting from proton donation of the catalyst species also causes skeletal rearrangements and fragmentation of the forming polybutene polymer. By comparison, in view of the evidence that the BF_3 tertiary etherate complexes of the present invention are capable of operating in an essentially completely anhydrous environment requiring no protic initiation, polymerization in accordance with the present invention is initiated in a substantially nonacidic environment which reduces acid catalyzed isomerization of vinylidene double bonds to di-, tri- and tetra-substituted internal double bonds. Also, fragmentation and skeletal rearrangements are minimized. As distinguished from a cationic mechanism, it is believed that polymerization in the present invention proceeds via a covalent mechanism.

A critical feature of the present invention which dictates the ability of the BF_3-etherates disclosed herein to produce high vinylidene polymer and to operate without necessity of protic initiation, is that the ether in the BF_3-etherate complexes must have at least one tertiary carbon bonded to the ether oxygen. BF_3-etherates which do not fulfill this requirement are outside the scope of the present invention and will not polymerize isobutylene in such a manner as to produce the very high levels of vinylidene possible in the present invention.

Detailed Description

The BF_3-tertiary etherates of the present invention can be prepared by reacting gaseous BF_3 with a tertiary ether under carefully controlled conditions of temperature and rate of reaction whereby the xothermicity of the BF_3-etherate complex formation is prevented from causing

the decomposition of the complex. In the case of the BF_3-methyl t-butyl ether or n-butyl t-butyl ether complexes, such decomposition would result in the formation of BF_3 methanol (or butanol) complexes with the release of isobutylene and dimers or trimers of isobutylene. To prevent such decomposition, gaseous BF_3 can be bubbled into the ether at a relatively slow rate over a period of about 1 to 5 hours and at a temperature not exceeding about 0°C. A preferred temperature to minimize breakdown of the etherate complex is about -60 to about -30°C. If desired, a further means of controlling the reaction between the BF3 and the ether is to dilute the BF_3 with an inert gas such as nitrogen and/or dilute the ether with inert solvents such as dichloromethane.

Ether having a tertiary carbon bonded to the ether oxygen can be used in the preparation of the BF_3-etherates of the present invention. Suitable ethers include methyl tertiary-butyl ether, ethyl tertiary-butyl ether, n-propyl tertiary-butyl ether, isopropyl tertiary-butyl ether, ditertiary-butyl ether, 1, 1'-dimethylbutyl methyl ether, and so on. The tertiary position of the ether is preferably a tertiary butyl group for smoothest initiation of polymerization and minimization of branching or skeletal rearrangement in isobutylene polymerization. Also, generally speaking, as the hydrocarbyl group (preferably alkyl) of the non-tertiary portion of the ether is increased from methyl to isopropyl to butyl, etc., the molecular weight of the resultant polybutene polymer is increased.

The mole ratio of ether to BF_3 in the etherates of the present invention should be in the range of about .5 to about 3:1. Preferably, to maximize attainment of high vinylidene content in the resulting polybutene polymer, the ether should be in at least a slight molar excess of the BF_3, most preferably in the range of about 1:1 to about 1.1:1. At mole ratios below about 1:1, the vinylidene content begins to decrease. Above about 1.1:1 little further improvement is observed.

The BF_3-etherates can be prepared ahead of time for subsequent use as a preformed catalyst complex, such as when polymerization is to be carried out in a batch process. In a continuous process the BF_3-etherates can be preformed in line immediately prior to entering the polymerization reaction. If performed ahead of time and stored for subsequent use, the BF_3 etherates should be maintained at 0°C or less to prevent decomposition.

The present invention is also directed to a process for polymerizing a feedstock comprising 1-olefins which process comprises contacting the feedstock with the BF_3-tertiary etherates described above.

The hydrocarbon feedstock may be pure 1-olefin or a mixture of 1-olefins. 1-olefin feedstock where the olefin contains 3 to 16 carbon atoms is preferred. If a pure olefin is used which is gaseous under ambient conditions it is necessary either to control the reaction pressure or to dissolve the olefin in a solvent medium inert under the reaction conditions in order to maintain the olefin in the liquid phase. In the case of isobutylene, which is typical of 1-olefins, the feedstock used in the polymerization process may be pure isobutylene or a mixed C_4 hydrocarbon feedstock such as that resulting from the thermal or catalytic cracking operation conventionally known as a butadiene or C_4 raffinate. This is a liquid when under pressure and hence no diluent is needed. The feedstock used may suitably contain between 5 and 100% by weight of isobutylene. It is preferred to use a feedstock containing at least about 10% by weight of isobutylene. The hydrocarbon feedstock used may contain, in addition to isobutylene, butanes and butanes without adverse effect on the polybutene product.

The polymerization temperature should be selected based on the molecular weight desired in the product. As is well known, lower temperatures can be used for higher molecular weights while higher temperatures can be used to obtain lighter products. The polymerization of the present invention can be carried out in the full range of temperatures generally associated with conventional polybutene polymerization, i.e., about -100°C to about +50°C. Polybutene molecular weights in the greatest commercial demand, i.e., those of molecular weight 100 to about 5000 can be obtained in the polymerization of the present invention at temperatures in the range of about -50°C to about +10°C.

The residence time required in the polymerization of the present invention represents an important advantage over the prior art which generally teaches short, strictly controlled residence times. For example, in Boerzel U.S. Patent 4,152,499, it is shown that residence times exceeding about 10 minutes are detrimental to the vinylidene character of the polymer. By comparison, typical residence times in the present invention range from about 10 minutes to 3 hours, while residence times of greater than 3 hours can be used to produce heavy polymer in reactions carried out at very low temperatures (i.e., -30° to -100°C). Such longer residence times are possible without the adverse effects upon vinylidene content noted in column 1 of the Boerzel '499 patent. Generally speaking, while the choice of residence time will be dictated in a known manner by factors such as the isobutylene concentration in the feed, temperature of reaction, catalyst concentration and the desired molecular

weight of the product, it should be pointed out that the residence time should not be allowed to extend longer than the time required for the isobutylene concentration in the feed to decrease to about 1 wt% (which can be readily monitored by gas chromatography). If allowed to continue beyond this point, the polymer is susceptible to isomerization of the desired vinylidene double bond to the less reactive tri- or tetra-substituted internal double bond.

The amount of BF_3-etherate used in the polymerization is not critical to the invention. Generally speaking, amounts ranging from at least about .01 mole percent based on isobutylene in the feed are suitable. About .05 to about 1 mole % is sufficient to obtain conversions of isobutylene of 80-90%. Generally speaking, raffinate feeds may require higher levels of the BF_3 complex than would suffice for a feed of pure isobutylene, to obtain 80-90% conversions. This is believed due to the number of competing reactions in the raffinate as opposed to synthetic feeds.

The polymerization of the present invention aided by the novel BF_3-tertiary etherates disclosed herein can be used to obtain a full range of polybutene molecular weights depending upon conditions of reaction time, feed, reaction temperature, etc. all of which can be controlled in a known manner. Polybutene obtained from the present invention having 80 to 100% vinylidene is more reactive than conventional polybutene having much lower vinylidene. As such the polybutene prepared in the present invention is particularly well suited for reaction with maleic anhydride to obtain valuable PIBSA intermediates useful in the manufacture of fuels and lubricant additives.

The following examples are intended for illustration only and should not be construed as limiting the invention set forth in the claims.

EXAMPLE I

Preparation of BF_3-Methyl-t-butyl Etherate

Into a 50 ml flask was charged 33 ml (.28 moles) of methyl-t-butyl ether (MTBE). The flask of ether was then cooled to -40°C. Gaseous BF_3 (6610 cc; .28 moles) was then slowly bubbled into the ether at a rate of 22 cc/min. with vigorous stirring. The gas phase of the flask was continually purged with nitrogen and the vent gases bubbled through 20% NaOH to remove acidic components. After addition of the BF_3 was complete, the gas phase of the flask was purged for another 20 minutes to ensure removal of free BF_3. The BF_3-methyl t-butyl etherate was stored at 0°C. until ready for use.

EXAMPLE II

Example I was repeated except that ethyl-t-butyl ether was used instead of MTBE.

EXAMPLE III

Example I was repeated using n-butyl-t-butyl ether.

EXAMPLE IV

Example I was repeated using isopropyl-t-butyl ether.

EXAMPLE V

Example I was repeated using di-t-butyl ether.

EXAMPLE VI

Example I was repeated using n-propyl-t-butyl ether.

EXAMPLE VII

Example I was repeated using isoamyl-t-butyl ether.

EXAMPLE VIII

Example I was repeated using 1, 1'-dimethylbutyl-methyl ether.

EXAMPLE IX

Example I was repeated using cyclohexyl-t-butyl ether.

EXAMPLE X

Example I was repeated using benzyl-t-butyl ether.

EXAMPLE XI

The BF_3-MTBE complex of Example I was used to polymerize a feed consisting of 20% isobutylene in isobutane. The feed contained less than 1.0 ppm water. Three separate batch polymerizations (summarized in Table 1 below) were run in an autoclave batch reactor equipped with a heat exchanger and in line cooling coils. The autoclave was cooled to the desired temperature followed by addition of 550 grams of the feed. The BF3-MTBE complex was charged to a pre-cooled stainless steel bomb attached to the reactor inlet. The complex was introduced into the reactor by purging the bomb with 50 grams of

the above-mentioned feed, followed by nitrogen to obtain a pressure in the reactor of 200 psi. The reaction conditions for each run are summarized in the Table 1 below. Each run produced colorless polybutene having at least 80% vinylidene content. Product olefin distribution (i.e., relative amount of vinylidene, tri-substituted and tetra-substituted double bond) was determined by ^{13}C NMR.

TABLE 1
Isobutylene Polymerization using BF_3-MTBE

Reaction Temp. (°C)	Mole % of Catalyst*	% Isobutylene Conversion	Mn	Mn
0	0.05	92	283	441
0	0.10	98	279	409
10	0.29	88	240	303

TABLE 1 (cont'd..)

Dispersion Index	^{13}C NMR Analysis		
	% Vinylidene	% Tri	% Tetra
1.56	80	17	3
1.59	81	16	3
1.26	81	16	3

* mole % of catalyst relative to isobutylene.

EXAMPLE XII

In a pilot plant continuous reactor cooled to -15°C, BF_3-MTBE was preformed by in-line mixing of BF_3 and methyl-t-butyl ether just prior to entering the reactor. The mole ration of ether to BF_3 was 1:1. The feed was a typical refinery C_4 raffinate (water washed and dried) containing 18% isobutylene and 5 ppm water. The catalyst load was 0.36 mole percent in relation to the washed feed. The colorless product (total polymer) had an olefin distribution of 74% vinylidene, 13% trisubstituted and 8% tetrasubstituted. The stripped polymer had 87% vinylidene, M_n=626, M_w=789, dispersion index=1.29 and a flash point ASTM D-92 COC) of 242°C.

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EXAMPLE XIII

The batch polymerization process outlined in Example XI was repeated except that BF_3-butyl-t-butyl etherate (Example II) was used instead of BF_3-MTBE. Table 2 below summarizes the reaction conditions and results for two separate runs. As in Example XI, the feed was 20% isobutylene in isobutane and virtually anhydrous (<1 ppm H_2O). Both runs were conducted at -18°C with a residence time of 60 minutes. The mole ratio of ether to BF_3 in the catalyst complex was 1.1:1.

TABLE 2

Isobutylene Polymerization Using BF_3-BTBE

Init. Conc.* of BTBE-BF_3	GPC Data Mn	Mw	DI
0.13	1228	2631	2.14
0.13	1419	2756	1.94

* The concentration of BTBE-BF_3 in mole % relative to isobutylene.

TABLE 2 (Cont'd.)

Olefin Distribution

13C NMR

% Vinylidene	% Trisubstituted	% Tetrasubstituted
87	8	5
93	7	0

EXAMPLE XIV

The batch polymerization of Example XI was repeated except that BF_3-butyl-t-ether(BF_3-BTBE) was substituted for BF_3-MTBE, and a water washed (and dried) refinery C4 raffinate was substituted for the 20% isobutylene in isobutane feed. Table 4 below summarizes the results of four separate runs. Each run was carried out at -18°C with a residence time of 40 minutes. Raffinate source "A" (Whiting) consisted of about 14% isobutylene and was dried to < 5 ppm H_2O. Raffinate source "B" (Texas City) consisted of about 18 / isobutylene and was dried to a moisture content of < 5 ppm H_2O. The mole ratio of butyl-t-butyl ether to BF_3 in the complex was 1.1:1.

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TABLE 3
Isobutylene Polymerization Using
BF_3:BTBE and C_4 Raffinate

Raffinate Source	Mol % Catalyst	GPC Data		
		Mn	Mw	DI
A	0.76	902	1534	1.70
A	1.01	916	1446	1.77
B	0.52	806	1842	2.29
B	0.78	569	1044	1.83

TABLE 3 (Cont'd.)
Olefin Distribution
13C NMR

% Vinylidene	% Trisubstituted	% Tetrasubstituted
84	12	4
80	17	3
81	14	5
80	15	5

EXAMPLE XV

Using the batch polymerization outlined in Example XI, with BF_3-BTBE catalyst, the effect on vinylidene content of varying the mole ratio of BTBE to BF_3 was studied in five separate runs summarized in Table 4 below. The feed was 20% isobutylene in isobutane (< 1 ppm H_2O), the reaction temperature was -18°C and the residence time was 40 minutes.

TABLE 4

Effect of Varying Mole Ratio of Ether to BF_3 Upon Vinylidene Content

Mole Ratio BTBE/BF3	Mol. % BTBE:BF3	Olefin Dist. ^{13}C NMR Vinylidene	Tri	Tetra
1:1	0.38	76	15	9
1.1:1	0.52	83	17	0
1:1	0.38	75	18	8
0.8:1	0.52	63	30	7
1.1:1	0.62	83	15	2

TABLE XVI

The batch polymerization of Example XI was repeated except that the BF_3 etherate was prepared from isopropyl-t-butyl ether (PTBE). The feed was 20% isobutylene in isobutene containing less than 1 ppm H_2O. Five runs were carried out using a reaction temperature of 0°C and a residence time of 50 minutes. The runs are summarized in Table 5 below.

TABLE 5

Isobutylene Polymerization Using BF_3:PTBE

Mole Ratio PTBE:BF_3	Mol % Catalyst	GPC Analysis Mn	Mw	DI
1.1:1	0.56	323	478	1.48
1:1	1.56	381	583	1.53
1.1:1	0.42	403	613	1.52
1.1:1	0.56	487	746	1.53
1:1	0.22	713	1272	1.78

TABLE 5 (Cont'd.)
Olefin Distribution
13C NMR

% Vinylidene	% Trisubstituted	% Tetrasubstituted
100	1	-
85	13	2
100	-	-
100	-	-
85	11	4

EXAMPLE XVII

For purposes of comparison, BF_3-ethanol and BF_3-butanol complexes were evaluated for their ability to produce polybutene having high vinylidene content. BF_3-ethanol and BF_3-butanol complexes were prepared using the general procedures of Example I as follows: Into a flask was charged 1.09 moles of ethanol or butanol. The flask was then cooled to 0°C with an ice bath. Gaseous BF_3 (1.09 moles) was bubbled into the flask with vigorous stirring over a period of about 120 minutes. The gas phase of the reaction vessel was continually purged with nitrogen and the vent gases bubbled through 20% NaOH to remove acidic components. Following addition of all the BF_3 the gas phase of the flask was purged with nitrogen for another 20 minutes to ensure removal of any free BF_3. The resulting BF_3 ethanol or butanol complexes were evaluated in a series of runs for polymerization of a feed consisting of 20% isobutylene in isobutane. In Table 6, below, the concentration of the BF_3-alcohol complex was .19 mole % based on the feed, the reaction temperatures were varied (9°C-1°C and -10°C) and the residence times were as long as necessary to react about 99% of the isobutylene, which in all of the runs was about 20 minutes. The batch polymerizations were carried out according to the procedures outlined in Example XI. Table 6 below summarizes the results of 3 BF_3-ethanol runs.

TABLE 6
Isobutylene Polymerization
Using BF_3-Ethanol Complex

Reaction Temp. °C	GPC Data Mw	Mn
9	500	300
-1	600	400
-10	1000	600

TABLE 6 (Cont'd.)
Olefin Distribution
13C NMR

% Vinylidene	% Trisubstituted	% Tetrasubstituted
76	22	2
73	24	3
80	17	3

A BF_3-butanol complex as prepared above was evaluated in four batch polymerization runs using 20% isobutylene in isobutane as the feed. The catalyst concentration was 0.18 mole %, residence times (allowing for reaction of 99% of the isobutylene in the feed) were 30 minutes and the reaction temperatures were -18°C, -12°C, 0° and 10°C. Table 7 below summarizes these four BF_3-butanol runs.

TABLE 7
Isobutylene Polymerization Using
BF_3-Butanol Complex

Reaction Temp. °C	GPC Data Mw	Mn
-18	1700	800
-12	1400	700
0	800	400
10°	450	300

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TABLE 7 (Cont'd.)

Olefin Distribution

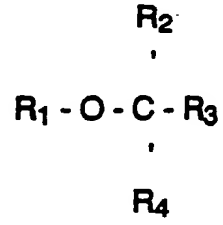
13C NMR

% Vinylidene	% Trisubstituted	% Tetrasubstituted
75	18	7
72	21	7
72	22	6
72	23	5

That which is claimed is:

1. A boron trifluoride etherate complex in which the ether of the complex has at least one tertiary carbon bonded to an ether oxygen.

2. The boron trifluoride etherate complex of Claim 1 wherein the ether has the general formula:



where R_1 is C_1 to C_{20} hydrocarbyl or halo-substituted hydrocarbyl, and R_2, R_3 and R_4, being the same or different, are selected from the group consisting of $-CH_2R'$, $-CH=R''$, and $-C\equiv R'''$ where R', R" and R"', the same or different are C_1 to C_{20} hydrocarbyl or halo-substituted hydrocarbyl.

3. The boron trifluoride etherate complex of Claim 2 wherein R_2, R_3 and R_4 are methyl.

4. The boron trifluoride etherate complex of Claim 3 wherein R_1 is selected from the group consisting of methyl, ethyl, propyl, isopropyl, butyl, isobutyl, and t-butyl.

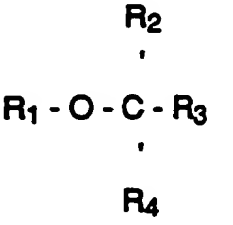
5. The boron trifluoride etherate complex of Claim 4 wherein R_1 is methyl.

6. The boron trifluoride etherate complex of Claim 4 wherein R_1 is butyl.

7. The boron trifluoride etherate complex of Claim 4 wherein R_1 is isopropyl.

8. A boron trifluoride etherate composition obtained by reacting an ether having at least one tertiary carbon bonded to an ether oxygen, with boron trifluoride, under conditions suitable to obtain a stable boron trifluoride etherate complex.

9. The boron trifluoride etherate composition of Claim 8 wherein the ether has the general formula:



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where R_1 is C_1 to C_{20} hydrocarbyl or halo-substituted hydrocarbyl and R_2, R_3 and R_4, being the same or different, are selected from the group consisting of $-CH_2R'$, $-CH=R''$, and $-C\equiv R'''$, where R' R" and R"', the same or different are C_1 to C_{20} hydrocarbon or halo-substituted hydrocarbyl.

10. The boron trifluoride etherate complex of Claim 9 wherein R_2, R_3 and R_4 are methyl; R is methyl, ethyl, propyl, isopropyl, butyl, isobutyl or t-butyl, and obtained by reacting the ether and boron trifluoride in a molar ratio of about .8 to about 3 to 1.

11 The boron trifluoride etherate complex of Claim 10 wherein the ratio is at least about 1 to 1.

12. The boron trifluoride etherate complex of Claim 10 wherein R_1 is methyl.

13. The boron trifluoride etherate complex of Claim 10 wherein R_1 is n-butyl.

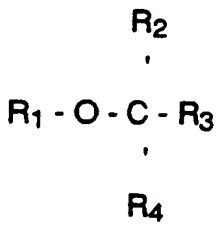
14. The boron trifluoride etherate complex of Claim 10 wherein R_1 is isopropyl.

15. The boron trifluoride etherate complex of Claim 10 wherein R_1 is t-butyl.

16. A process for polymerization of a feedstock containing a 1-olefin or mixture thereof which process comprises the step of contacting the feedstock with a boron trifluoride etherate complex wherein the ether of the complex has at least one tertiary carbon bonded to an ether oxygen.

17. The process of Claim 16 wherein there is obtained polybutene having a vinylidene content of at least about 80%.

18. The process of Claim 16 wherein the boron trifluoride etherate has the general formula:



where R_1 is C_1 to C_{20} hydrocarbyl or halo-substituted hydrocarbyl and R_2, R_3 and R_4, being the same or different are selected from the group consisting of $-CH_2R'$, $-CH=R''$, and $-C\equiv R'''$, wherein R' R" and R"', the same or different are C_1 to C_{20} hydrocarbyl or halo-substituted hydrocarbyl.

19. The process of Claim 18 wherein R_2, R_3 and R_4 are methyl.

20. The process of Claim 19 wherein R_1 is selected from the group consisting of methyl, ethyl, propyl, isopropyl, butyl, isobutyl, t-butyl.

21. The process of Claim 20 wherein R_1 is methyl.

22. The process of Claim 21 wherein the etherate is the reaction product of the ether and boron trifluoride reacted in a mole ratio of at least about 1:1.

23. The process of Claim 20 wherein R_1 is butyl.

24. The process of Claim 23 wherein the etherate is the reaction product of the ether and boron trifluoride reacted in a mole ratio of at least about 1:1.

25. The process of Claim 20 wherein R_1 is isopropyl.

26. The process of Claim 25 wherein the etherate is the reaction product of the ether and boron trifluoride reacted in a mole ratio of at least about 1:1.

27. The process of Claim 19 wherein there is produced polybutene having a vinylidene content of at least about 80%.

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INTERNATIONAL SEARCH REPORT

International Application No. PCT/US91/08640

I. CLASSIFICATI N F SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

INT CL[5] C07C 2/08, B01J 21/02, C01B 35/06
U.S. CL 585/525, 502/203, 423/293

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
U.S.	585/525, 502/203, 423,293

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category [10]	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
A	US, A, 2,559,062 (DORNTE) 03, July 1951, See column 1, lines 25-41, column 5, lines 41-61	1-27
A	US, A, 2,780,664 (SERNIUK) 05, February 1957, See column 2, lines 9-33	1-15
X	US, A, 4,098,983 (OSBORN ET AL) 04, July 1978, See column 11, line 58, column 3, lines 51-66	1-15
A	US, A, 4,859,572 (CHEN ET AL) 18, July 1989, See column 10, lines 34-51 and 66-68, column 11, lines 1-2 column 4, lines 17-21	1-27
X	GB, A, 804,070 (Esso Research and Engineering Company) 17, May, 1957, page 2, lines 29-93	1-5,8,9
X	CA, A, 576,759 (Esso Research and Engineering Company) 26, May 1959, See page 3, columns 13-21	1-5,8,9

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATI N

Date of the Actual Completion of the International Search

27 May 1992

Date of Mailing of this International Search Report

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International Searching Authority

ISA/US

Signature of Authorized Officer

P. Achutamurthy

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